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COMPLEX THINNER BASED ON SODA, LIQUID GLASS AND OXYETHYLIDENEDIPHOSPHONIC ACID IN CERAMIC CASTING TECHNOLOGY

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The effect of a complex thinner based on soda, liquid glass and oxyethylidenediphosphonic acid on the rheological and casting properties of the Stephan Schmidt 13250 clay suspension and on the mechanical properties of dried and fired samples was studied. The additive makes it possible to decrease the moisture content of clay suspensions while preserving their performance. The strength and density of dry and fired clay samples are increase while the shrinkage and porosity decrease.

Key words: ceramic slip, rheology, clay suspension, thinning additive, thixotropy, oxyethylidenediphosphonic acid.

Slip casting of water suspensions is used in the production of ceramic sanitary wares. The quality of the wares largely depends on how successfully the problem of matching the technological settings of the casting program and the slip parameters is solved. For this reason the key problem of this technology is the preparation of slips whose properties satisfy the high rate of structure formation and buildup of the strength of the clay piece [1].

Stephan Schmidt 13250 clay from the company Stephan Schmidt Group (Germany) is used in slip casting in Russia and other countries. In terms of the mineralogical composition this clay is a kaolinite-hydromica with an admixture of quartz and has the following chemical composition (wt.%[3]): SiO_2 — 69.2; Al_2O_3 — 24.0; TiO_2 — 1.5; Fe_2O_3 — 1.4; CaO — 0.2; MgO — 0.4; K_2O — 1.9; Na_2O — 0.2; other — 8.7.

The thinner, which is added to give the suspension the necessary rheological parameters, plays a special role in the dissolution of the clay. Specifically, it is necessary to obtain a suspension with the highest possible fluidity and a sufficiently high concentration of the solid phase. In the ceramic industry the standard components of the thinner are soda and liquid glass. The efficacy of a complex thinner can be increased by introducing into it additional components that improve the structural-mechanical properties of the slip, for example, oxyethylidenediphosphonic acid (OEDPA, empirical formula $C_2H_8O_7P_2$), which has performed well in some ceramic technologies [2, 3]. The combination of two phosphonic groups in the OEDPA molecule promotes the formation of complexes with alkali and alkali-earth cations with high values of the stability constants [4].

As a result of previous investigations [5] it was determined that a ternary system based on soda, liquid glass and OEDPA decreases the viscosity and thixotropy of a suspension of Stephan Schmidt 13250 clay, and using methods of mathematical planning the compositions of this complex thinner were optimized.

The aim of the present work is to study the physical-chemical aspects of the action of the complex addition on the rheological and casting properties of the Stephan Schmidt 13250 clay suspension and on the mechanical properties of the molded dried and fired samples obtained from the suspensions studied and to determine the mechanism of the action of the additive.

Thinning additives with the compositions presented in Table 1 were prepared to study the rheological properties of the clay suspensions. We note that the two-component composition No. 1 is currently used in production and we recommended the compositions Nos. 2 and 3 in a previous work [5].

The measurements were performed in a RHEOTEST RN rotational viscometer and with the same moisture content (35%) of the clay suspension and constant temperature 25°C. The results, which were fit by the Bingham–Shvedov equation ($\tau = \tau_0 + \eta\gamma$, where τ is the shear stress, τ_0 is the maxi-

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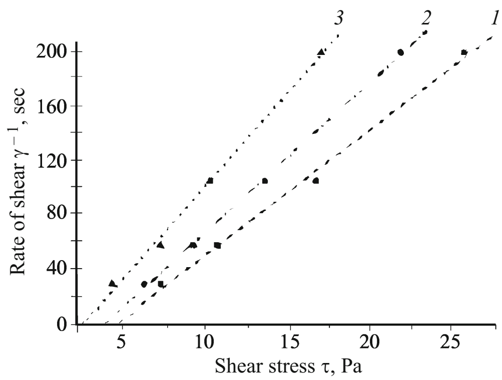

Fig. 1. Rheological curves for suspensions with additives: *1*) No. 1; *2*) No. 2; *3*) No. 3.

mum shear stress, η is the plastic viscosity, γ is the shear rate), are displayed in Fig. 1. The computed parameters are presented in Table 2.

It is evident from Table 2 that the addition of OEDPA to the thinner significantly lowers the rheological parameters and the rheological properties of the suspensions approach the rheological properties of Newtonian systems. Specifically, a reduction of τ_0 shows that the character of the flow changes from typical for structured systems to typical for free-disperse systems.

The rate of mass buildup was determined by a procedure using gypsum rods [6]. Since it was determined in [5] that the No. 2 suspension with additive is more stable against aggregation than the No. 3 suspension with additive, suspensions with additive Nos. 1 and 2 were chosen for these studies. The average values of the mass buildup rate for the suspensions Nos. 1 and 2 (with constant moisture content $W = 35\%$) were 0.43 ± 0.01 and 0.37 ± 0.02 g/(cm^2 · min), respectively. It is evident that OEDPA lowers the mass buildup rate. The mass buildup rate can be increased by lowering the moisture content of the suspension, which makes it possible to increase the post-casting and -drying density of the samples. For this, it was established by adjusting the fluidity of the suspension using a Ford cup that the No. 2 suspension with additive and $W = 33\%$ has the same viscosity and thixotropy as the No. 1 suspension with $W = 35\%$. The mass buildup rate measured for the No. 2 suspension with moisture content 33% was 0.43 ± 0.02 g/(cm^2 · min).

To investigate the effect of a complex thinner on the drying and firing properties of clay bodies, tile samples were prepared by plastic molding from filtered suspensions with additives Nos. 1 and 2. The molded samples were dried in air for 24 h and then for 5 h in a drier at temperature 110°C. The dried samples were fired in a muffle furnace at temperature 1050°C for 4 h.

The air and fire shrinkage were found by varying the distance between markers on the samples after drying and firing. An FM-250 fracture machine was used to determine the ultimate strength of the samples in three-point bending.

It can be concluded from the results of physical-mechanical tests (Table 3) that OEDPA addition to the thinner composition increases strength for dry and fired samples. Samples with additive No. 2 show smaller shrinkage compared with samples with additive No. 1.

The IR spectra of the clay suspensions studied (Avatar 360 ESP IR spectrometer) are presented in Fig. 2. It follows from the spectra in which changes in the vibrational modes are not observed that complex additives have no effect on the structural properties of the clay particles.

The results of the investigation of the granulometric composition and ξ-potential of clay particles for all suspensions studied (Zetasizer Nano Laser Analyzer, Malvern Instruments) are presented in Figs. 3 and 4, respectively. The data presented in Fig. 3 show that the OEDPA addition to a complex additive has no effect on the granulometric composition. It follows from Fig. 4 that positively charged particles are present in a suspension of pure clay. After the production

TABLE 1. Compositions of the Thinning Additive

Additive	Composition of thinning additive, wt.%		
	No. 1	No. 2	No. 3
Soda	0.500	0.500	0.500
Liquid glass	0.072	0.042	0.072
OEDP	–	0.572	0.372

TABLE 2. Rheological Characteristics of Suspensions with Additives

Parameter	Suspensions with additives		
	No. 1	No. 2	No. 3
Plastic viscosity η, Pa · sec	0.110 ± 0.006	0.093 ± 0.002	0.074 ± 0.004
Maximum shear stress τ_0, Pa	5.3 ± 0.6	4.4 ± 0.2	2.9 ± 0.4

TABLE 3. Mechanical Properties of Air-Dry and Fired Samples

Parameter	Sample	
	with additive No. 1	with additive No. 2
Air linear shrinkage, %	8.1 ± 0.5	8.5 ± 0.5
Strength of dry samples, MPa	2.8 ± 0.2	4.3 ± 0.2
Fire linear shrinkage, %	6.2 ± 0.6	4.2 ± 0.6
Total linear shrinkage, %	14.3 ± 0.9	12.5 ± 0.9
Strength of fired samples at 1050°C, MPa	19 ± 2	28 ± 2
Water absorption, %	9 ± 1	8 ± 1
Bulk mass of fired samples, kg/m^3	1780 ± 80	1900 ± 80

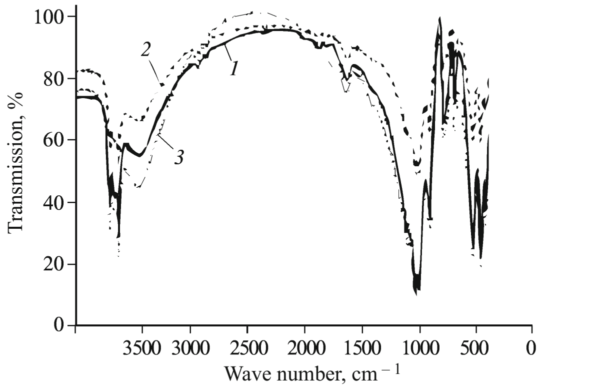

Fig. 2. Infrared spectra of suspensions: *1*) without additives; *2*) with additive No. 1; *3*) with additive No. 2.

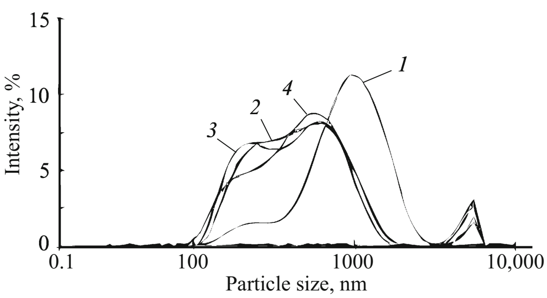

Fig. 3. Data from granulometric analysis of clay suspensions: *1*) without additives; *2*) with additive No. 1; *3*) with additive No. 2; *4*) with additive No. 3.

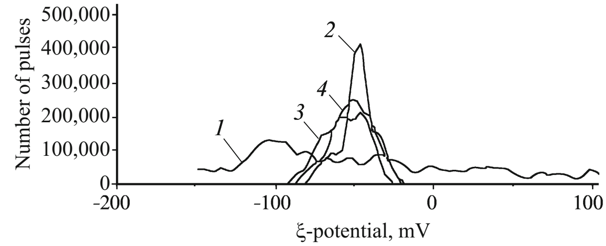

Fig. 4. Distribution of the ξ-potential in clay suspensions: *1*) without additives; *2*) with additive No. 1; *3*) with additive No. 2; *4*) with additive No. 3.

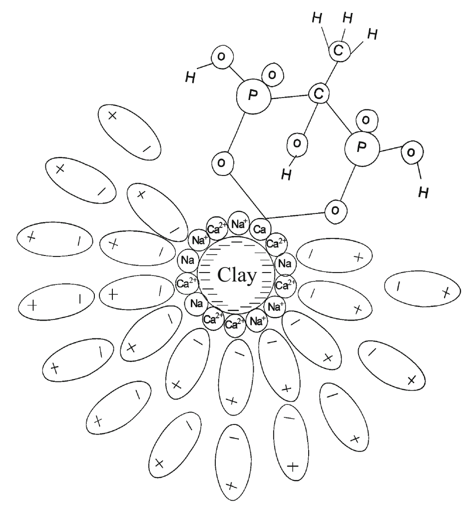

Fig. 5. Schematic representation of the chemosorption of OEDPA on clay particles.

additive is introduced they completely vanish and the ξ-potential increases in modulus. Therefore, the hydrate shell around a clayey particle increases and the stability of the suspension increases. The introduction of OEDPA increases the ξ-potential very little compared with the production additive. The average values of the ξ-potential (mV) for all the suspensions studied are as follows:

–17.5 — no additive;
–47.9 — with additive No. 1;
–53.2 — with additive No. 2;
–53.3 — with additive No. 3.

In summary, it is our opinion that ion-exchange and chemosorption determine the effect of a complex additive consisting of soda, liquid glass and oxyethylidenediphosphonic acid on the rheological properties of a clay suspension. When these components are mixed the complexonate Na_2OEDP is formed, and in solution it dissociates into the anion $[OEDP]^{2-}$ and the cations Na^+ [4]. For a thinner based on soda and liquid glass the mechanism of ion-exchange with the participation of Na^+ and Ca^{2+} ions in the volume of the suspension and on the surface of clay particles is presented in the literature [7]. In the complex additive, in view of the much higher stability of the complexes Ca[OEDP] compared with Na_2OEDP [4], the anion $[OEDP]^{2-}$ interacts with the cation Ca^{2+} on the surface of a clay particle (Fig. 5), as a result of which the surface charge of clay particles becomes more negative (the ξ-potential increases in modulus). Owing to the chelation effect the anion $[OEDP]^{2-}$ forms in the volume of the suspension undissociated compounds with calcium ions [4]. These suppositions are confirmed by the observed reduction of the viscosity of suspensions on introduction of OEDPA.

The increase in the strength of dry samples when complex thinner is introduced into the slip composition can be explained by the fact that Ca[OEDP] undergoes polymerization during the drying process [4]. However, the increase in strength of the samples after firing is explained by the fluxing action of calcium phosphate compounds.

CONCLUSIONS

It was proved in the present investigation and in [5] that the action of a complex filler based on soda, liquid glass and oxyethylidenediphosphonic acid in the technology for the production ceramic articles by casting is effective: the clay dissolution time decreases and the viscosity and thixotropy

of the suspension decrease to minimal values. To explain the changes in the structural-mechanical properties of the suspensions a mechanism was proposed for the action of the complex additive that includes ion-exchange, complex formation and chemosorption. It was determined that the complex additive makes it possible to decrease the moisture content of the suspension by 2% while preserving the working parameters of the suspension. An increase in the strength and density of dry and fired clay samples as well as a decrease in the shrinkage and porosity are observed. In summary, the complex additive makes it possible to optimize the technology at the stages of preparation of the casting slip and to decrease the number of parts rejected during molding, drying and firing.

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